An investigation of WC stability during the preparation of Pt@WC/OMC via a pulse microwave assisted polyol method

Kun Wang [a], Zhangweihao Pan [a], Fotini Tzorbatzoglou [c], Yueli Zhang [a], Yi Wang [b,**], Panagiotis Tsiakaras [c,***], Shuqin Song [a,*]

[a] State Key Laboratory of Optoelectronic Materials and Technologies/The Key Lab of Low-carbon Chemistry & Energy Conservation of Guangdong Province, School of Physics and Engineering, Sun Yat-sen University, Guangzhou, 510275, China
[b] School of Chemistry and Chemical Engineering, The Key Lab of Low-carbon Chemistry & Energy Conservation of Guangdong Province, Sun Yat-sen University, Guangzhou 510275, China
[c] Department of Mechanical Engineering, School of Engineering, University of Thessaly, Pedion Areos 38834, Greece

ARTICLE INFO

ABSTRACT

In the present work, the WC stability during the preparation of Pt@WC/OMC (Ordered Mesoporous Carbon) electrocatalysts, through a pulse microwave-assisted polyol method, is investigated by the aid of X-ray diffraction and thermogravimetric method. More precisely, OMC self-supported tungsten carbide (WC/OMC) is successfully synthesized by combing the hydrothermal process and a hard template method and its stability is step by step checked during the preparation process of the Pt@WC/OMC electrocatalyst by the pulse microwave-assisted polyol method.

It is found that the strong alkaline and acid environment has a relatively small but not serious effect on the stability of WC. It is also found that in absence of Pt precursor, microwave irradiation itself also has a small effect on the stability of WC, while once Pt precursor is introduced into the system, more than half of the initial WC disappears or is oxidized. To avoid this process, Pt@WC/OMC-MM is obtained by mechanically mixing (MM) the as prepared WC/OMC and Pt@C. Moreover, the electrochemical results of methanol oxidation reaction show that the content of WC has an obvious effect on Pt's activity toward MOR, with the best performance in the case of $Pt_{20}WC_{22}/OMC$-MM.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Tungsten carbide (WC), since Levy and Boudart [1] demonstrated its catalytic properties similar to Pt, has been proved to be a very promising alternative electrocatalyst [2–6] for fuel cell application. The special characteristics of WC in electrocatalysis, such as the excellent tolerance to CO and H_2S [7–9], the desirable synergistic effect on Pt's activity toward the electrooxidation of both hydrogen [10] and methanol [11–14], as well as toward the oxygen reduction reaction [15–21], have already been recognized. These properties make WC an interesting and attractive low-cost electrocatalyst alternative. Moreover, WC exhibits good stability in both acidic and alkaline media, under different electrochemical conditions [22–27].

The corresponding investigations on WC stability in variable harsh conditions, such as strong base or acid environment [24], high temperature [23] and potential cycling [28], have been carried out. On the other hand, it is known that WC alone is inactive or less active to the electrochemical reactions [29]. For this reason, Pt-based particles are always deposited on WC or on carbon supported WC, leading to an increased electrochemical activity through the synergetic effect [4,29,30]. Recently, Zheng et al. [3] reported that WC/OMC composites were active and exhibited very close performance to Pt for *methanol electrooxidation reaction* (MOR). Additionally, Lu et al. [2] indicated that WC not only played the role of support in Pt-based electrocatalysts, but also it constituted an active phase for MOR.

In any case, during the supported catalyst preparation process, in order to deposit and reduce the metal precursors, alkaline environment (or other deposition agents) and high temperature are always required [31–33]. Furthermore, in the colloid method for catalysts preparation, acid is needed to destroy the colloid and thus accelerate the deposition of metal particles [34,35]. Obviously, the general catalysts preparation process always involves wild conditions, which could lead to the instability of WC, in the case that

* Corresponding author. Tel.: +86 20 84113253; fax: +86 20 84113253.
** Corresponding author. Tel.: +86 20 84110930; fax: +86 20 84110927.
*** Corresponding author. Tel.: +30 24210 74065; fax: +30 24210 74050.
E-mail addresses: wangyi76@mail.sysu.edu.cn (Y. Wang), tsiak@uth.gr (Panagiotis Tsiakaras), stsssq@mail.sysu.edu.cn (S. Song).
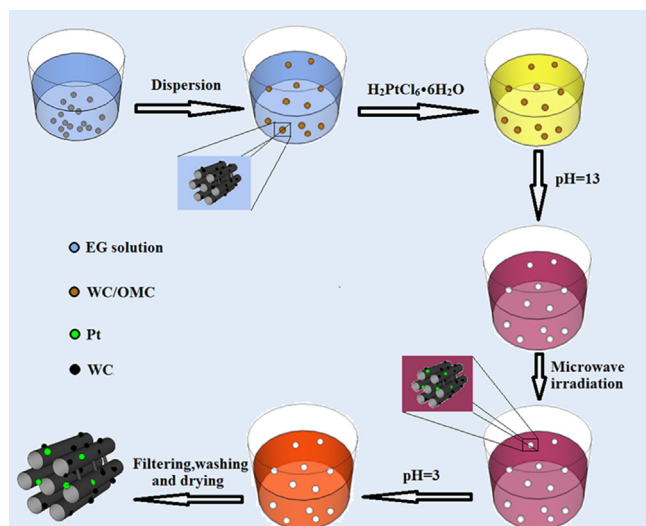
Fig. 1. The schematic procedure for Pt@WC/OMC preparation through a pulse microwave assisted polyol method.

it is adopted as the supporting materials. The microwave-assisted polyol method is one of the most desirable techniques for preparing supported Pt-based catalysts, because of the fast (∼2 min) and efficient reduction of the metal precursors to metal atoms [36–41].

The main advantages of this method derive from the microwave heating itself, which include: (i) speeding up (minutes instead of hours), (ii) high efficiency, (iii) high uniformity, and (iv) precise temperature regulation and control. The as-referred typical preparation process, as shown in Fig. 1, involves strong alkaline environment for metal precursor deposition and strong acid environment for destroying the colloid, and thus promoting the metal particles to settle onto the supported materials.

Additionally, in order for the metal ions to be completely reduced, high temperature (here in the form of pulse microwave irradiation) is required, especially in the case that ethylene glycol is used as the reducing agent.

In the present investigation, the stability of the as-prepared (via the combination of a hydrothermal process and a hard template method) *ordered mesoporous carbon self-supported tungsten carbide* (WC/OMC) composites is step by step and systematically studied during the preparation process of Pt@WC/OMC via a pulse microwave-assisted polyol method.

2. Experimental

2.1. Synthesis of WC/OMC composites

WC/OMC sample was prepared by combing the hydrothermal reaction and the hard template method with ammonium metatungstate (AMT) as the tungsten precursor, glucose as the carbon source and the ordered mesoporous silica (SBA-15) as the hard template, respectively. The preparation details have been previously described [14].

2.2. Preparation of electrocatalysts

The Pt@WC/OMC-MP (Microwave-Polyol method) catalyst with a Pt loading of 20 wt.% was prepared by a pulse microwave-assisted polyol method [42]. The preparation procedure, as shown in Fig. 1, can be described in details as follows. The as-prepared WC/OMC as the supporting materials was well mixed with *ethylene glycol* (EG) in an ultrasonic bath and then an appropriate amount of $H_2PtCl_6 \cdot 6H_2O$ dissolved in EG was added into the mixture.

After the pH value of the above mixture was adjusted to 13 by the dropwise addition of $1.0 \, mol \, L^{-1}$ NaOH/EG solution, the well-dispersed slurry was obtained with magnetic stirring for another 1 h. Thereafter, the slurry was microwave-heated in the pulse form of 10 s-ON/10 s-OFF for several times. After reaction, $1.0 \, mol \, L^{-1}$ HCl aqueous solution was added to accelerate the deposition process of metal particles. Finally, the resulting sample was filtered, washed with abundant hot water (≥90 °C) until no chloride anion was detected by $1.0 \, mol \, L^{-1}$ AgNO$_3$ solution in the filtrate, and then dried at 80 °C overnight in a vacuum oven.

In order to control WC content in the catalyst and compare with the activity of Pt@WC/OMC-MP, mechanical mixing method was adopted to obtain Pt@WC/OMC-MM (Mechanical Mixing) with different WC content. Pt@C catalysts were prepared by a pulse microwave-assisted polyol method. Then, the as-prepared Pt@C catalysts were mixed with the as-prepared WC/OMC by grinding for 2 h and then stirring in EG for 24 h. Next, the resulting sample was filtered, washed and then dried at 80 °C overnight in a vacuum oven. Finally, $Pt_{20}@WC_{17}/OMC$-MM, $Pt_{20}@WC_{22}/OMC$-MM and $Pt_{20}@WC_{27}/OMC$-MM were obtained ($Pt_x@WC_y/OMC$-MM, here the subscript is the weight percent and MM means the sample was obtained by mechanical mixing).

2.3. Physico-chemical characterization of WC/OMC

The low-angle and wide-angle *X-ray diffraction* (XRD) patterns were recorded on a D-MAX 2200 VPC diffractometer using Cu K$_\alpha$ radiation (30 kV, 30 mA). N$_2$ adsorption–desorption measurements were carried out using a Micromeritics ASAP 2010 analyzer at 77 K. The BET surface area (S_{BET}) and the mesopores volume (V_{mes}) were determined by the BET theory and Barrett–Joyner–Halenda (BJH) method, respectively. The *transmission electron microscopy* (TEM) investigations were performed by a JEOL TEM-2010 (HR) operating at 120 kV. *X-ray photoelectron spectroscopy* (XPS) characterization was performed by an ESCALAB 250.

2.4. Stability investigation of WC/OMC

In order to check the stability of the as-prepared WC/OMC (WC/OMC-0), the corresponding WC/OMC samples were treated through the following process without (a) or with (b) Pt precursor: (i) immersion in alkaline EG solution (pH = 13.0) for 3 h (WC/OMC-1a and WC/OMC-1b), (ii) after immersion in alkaline EG solution, microwave irradiation in the pulse mode of 10 s-ON/10 s-OFF for 5 times (WC/OMC-2a and WC/OMC-2b), (iii) after the above two steps, immersion in acidic solution (pH = 3.0) for 3 h (WC/OMC-3a and WC/OMC-3b). For the sake of clarification, the above treatment process is illustrated in Fig. 2. For the determination of WC content in the WC/OMC composite material, *thermogravimetric* (TG) experiments were carried out with a Netzsch TG-209 analyzer in air with a flow rate of 20 mL min^{-1} and a temperature ramp of 10 °C min^{-1}.

2.5. Electrochemical characterization

All the electrochemical measurements were conducted on an AUT84480 instrument in a three-electrode cell with a *saturated calomel electrode* (SCE) and a Pt foil (1.0 cm × 1.0 cm) as the reference and counter electrode, respectively. The thin catalyst film was prepared onto the glassy carbon disk surface with a diameter of 0.5 cm. Typically, a mixture containing 5.0 mg electrocatalyst, 1.80 mL ethanol and 0.20 mL Nafion solution (5 wt.%, density: 0.874 g mL^{-1}@25 °C, DuPont, USA) was ultrasonicated for 10 min and then stirred for 40 min to obtain a well-dispersed ink. The catalyst ink (10 μL) was then quantitatively transferred onto the surface of the glassy carbon disk electrode and dried under infrared lamp to obtain a catalyst thin film. The Pt loading was maintained
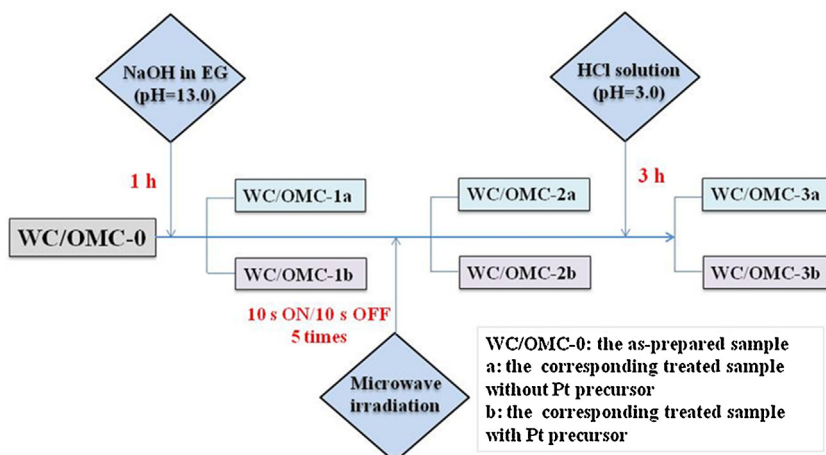
Fig. 2. The treated WC/OMC samples in the same procedure for the supported Pt catalyst preparation by the pulse microwave assisted polyol method.

to be 25.5 μg Pt cm^{-2}. It should be noted that all the potential was referred to the SCE without specification.

3. Results and discussion

3.1. Physicochemical characterization

The corresponding physico-chemical properties of the as-prepared WC/OMC are shown in Fig. 3. The respective diffraction peaks at 31.4°, 35.6°, and 48.4° in the wide angle XRD correspond

Fig. 3. XRD patterns of WC/OMC sample (A), and its N$_2$ adsorption–desorption isotherms (B) and the corresponding BJH pore size distribution and low-angle XRD patterns and TEM images of WC/OMC sample (inset of B).

to (0 0 1), (1 0 0) and (1 0 1) facets of WC (Fig. 3A), indicating that WC has been successfully synthesized. As seen from the low-angle XRD patterns of WC/OMC (the inset of Fig. 3B), WC/OMC exhibits an intense diffraction peak (10), demonstrating the formation of a highly ordered 2D hexagonal mesostructure [43,44]. This characteristic can be further verified by the parallel arranged channels observed from the TEM image (the inset of Fig. 3B). Typical IV nitrogen adsorption/desorption isotherms with distinct hysteretic loop (Fig. 3B) indicate the mesoporous structure of WC/OMC. The BET surface area and mesopore volume of WC/OMC are 409 m^2 g^{-1} and 0.47 cm^3 g^{-1}, respectively. Obviously, the WC/OMC has a big enough specific surface area to load metal particles with high dispersion. The pore size distribution through the BJH method clearly displays a unimodal, narrow pore size distribution with a peak pore diameter at about 5.0 nm for WC/OMC. Based on the above results, it is obvious that the ordered mesoporous WC/OMC composites have been successfully synthesized through combing the hydrothermal reaction and the hard template method.

Thermogravimetric analysis has already been adopted to determine the Pt content in carbon and nitrogen doped carbon supported Pt catalysts by using the weight of the final products PtO$_2$ [45,46]. TG is also tentatively used to quantify WC content in the WC/OMC composite material in the present work. In order to achieve this purpose, it should be to know what the final product of WC/OMC is after TG measurement. For this issue, the as-prepared WC/OMC was heat-treated under air at a flow rate of 20 mL min^{-1}, with temperature ramped from room temperature to 900 °C at 10 °C min^{-1}, which were the same operation parameters as those of TG analysis.

The XRD results shown in Fig. 4A clearly indicate that the main products of the heat-treated WC/OMC under the same TG operation conditions are WO$_3$, with little WO$_{3-x}$. For the further check of the final state of the sample after TG operation, XPS for the products of the heat-treated WC/OMC under the same conditions of TG operation was also collected. As shown in Fig. 4B, the W$_{4f}$ spectra can be deconvoluted into two pairs of doublets (W$_{4f5/2}$ and W$_{4f7/2}$). The strong peaks located at 35.91 eV and 38.06 eV are corresponding to WO$_3$ oxidation state, while the weak peaks located at 35.41 eV and 37.56 eV are corresponding to WO$_{2.5}$ oxidation state [13,47–49].

Considering the much bigger atomic weight of W (184) than that of O (16) and much lower content of WO$_{3-x}$ with respect to that of WO$_3$, even if the WC content determination is just based on WO$_3$ as the only residue in TG analysis, the measurement error can be neglected. As it can be seen from Fig. 4C, setting the weight of the anhydrous material to be 100 wt.%, with WO$_3$ as the final product for the calculation basis, the content of WC in the
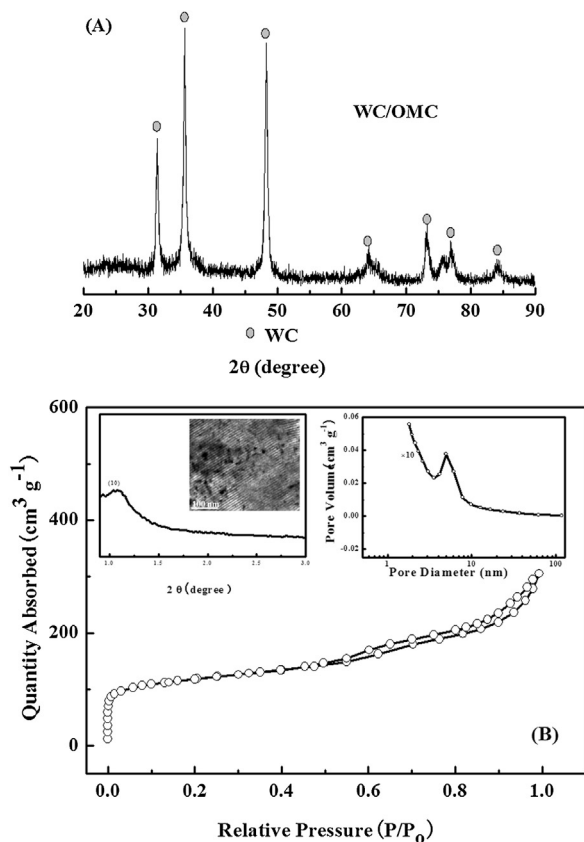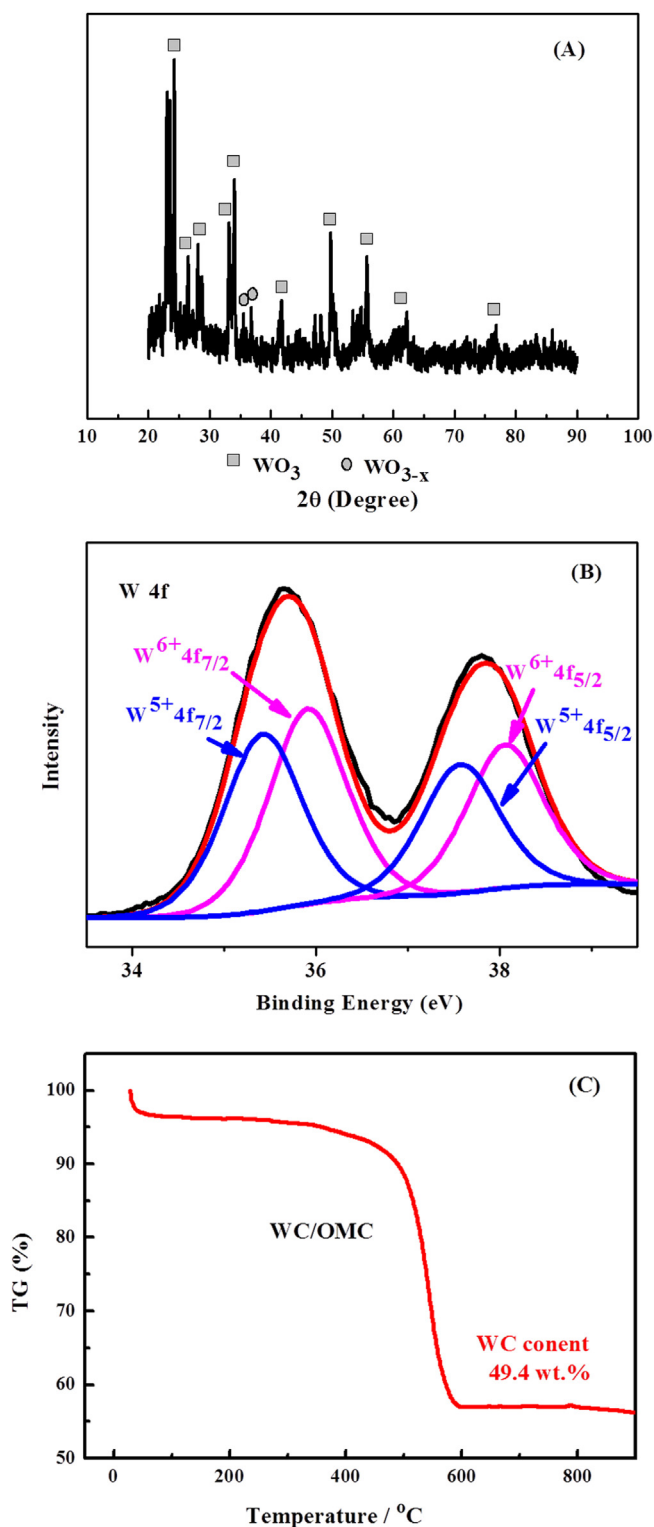
Fig. 4. XRD (A) and XPS (B) of the heat-treated WC/OMC sample under the same operation conditions as those of TG test and the thermogravimetric curves of the as-prepared WC/OMC for WC quantitative determination (C).

as-prepared WC/OMC is 49.4 wt.%. Based on the above discussion, TG analysis can be used for the determination of WC content in the WC/OMC composite material and then for its stability investigation during its supported Pt catalysts preparation through the pulse microwave assisted polyol method.

3.2. Investigation of WC/OMC stability

In order to investigate the stability of WC/OMC in the catalyst preparation process through the pulse microwave assisted polyol method, in each step which could affect the stability of WC (Fig. 2), the sample was filtered, washed, dried and then evaluated. The wide-angle XRD patterns of treated WC/OMC samples (Fig. 5A) reveal that the diffraction peaks of WC still maintain in the catalyst preparation process in the absence of Pt precursor. While, in the presence of Pt precursor, the diffraction peak intensity of WC becomes obviously weaker after microwave irradiation (Fig. 5B). To further explore the possible reasons, TG was carried out to quantify WC content in the sample. As shown in Fig. 5A′, in the case of without Pt precursor, WC loss is almost similar, from the initial 49.4 wt.% to about 40 wt.%, even WC/OMC-0 was treated through all the catalyst preparation process. This phenomenon indicates not only alkaline or acidic environment but also the microwave irradiation has a little effect on WC stability in absence of Pt precursor. While, in the presence of Pt precursor, before microwave irradiation, the WC loss is similar to the previous case. On the other hand, once microwave irradiation is provided, WC loss becomes significant, from 49.4 wt.% to less than 20 wt.% (Fig. 5B′). With the further treatment by acid, no further WC loss happens. This indicates that the existence of Pt can induce the dissolution or oxidation of WC in the microwave irradiation process. One can easily infer that the step of microwave irradiation in the presence of Pt precursor during the catalysts preparation process is the most serious parameter that leads to WC loss. Here it is worth noting that if the catalysts were prepared through the pulse microwave assisted polyol method, in the Pt@WC/OMC sample, W can be found in the form of WC and WO_3, which could be seen from the XPS results shown in Fig. 6. Obviously, part of WC has been oxidized into WO_3 during Pt@WC/OMC catalyst preparation. So, based on TG method, the real WC content in Pt@WC/OMC should be less than the calculated value.

3.3. Electrochemical characterization: methanol electrooxidation reaction

Considering the issue of WC loss in the catalyst preparation process and the contributing effect of WC on Pt's electrocatalytic activity, in order to take good advantage of the synergetic effect of WC, the as-prepared WC/OMC-0 was mechanically mixed with the as-prepared Pt@C to obtain $Pt_{20}@WC_{22}$/OMC (denoted as $Pt_{20}@WC_{22}$/OMC-MM). $Pt_{20}@WC_{21}$/OMC-MP (here the subscript 21 is the calculated WC weight percent from TG results, while the real WC content should be less than 21 wt.% as discussed above) was prepared through the normal pulse microwave assisted polyol method as the counterpart. Both were tested for MOR and the results are shown in Fig. 7. Not only the onset potential but also the specific mass activity on $Pt_{20}@WC_{22}$/OMC-MM is superior to those on $Pt_{20}@WC_{21}$/OMC-MP. In more details, the peak value of the specific mass activity of the $Pt_{20}@WC_{22}$/OMC-MM is about 488 mA mg_{Pt}^{-1}, much higher than the corresponding value (354 mA mg_{Pt}^{-1}) of the $Pt_{20}@WC_{21}$/OMC-MP. Our present result has a comparable result to that (410 mA mg_{Pt}^{-1}) on Pt supported on WO_3/OMC [50]. This could be attributed to the decreased crystallization of WC due to part of WC dissolution and WO_3 existence, produced from the oxidation of WC during the preparation of $Pt_{20}@WC_{21}$/OMC-MP. This can be clearly seen from the weaker diffraction peaks for WC in $Pt_{20}@WC_{21}$/OMC-MP with respect to those in $Pt_{20}@WC_{22}$/OMC-MM (Fig. 8). One might further conclude that the content of WC can affect the activity of Pt@WC/OMC to some extent.

For the further optimization of WC content in the catalysts, different Pt@WC/OMC-MM catalysts with the same Pt loading but
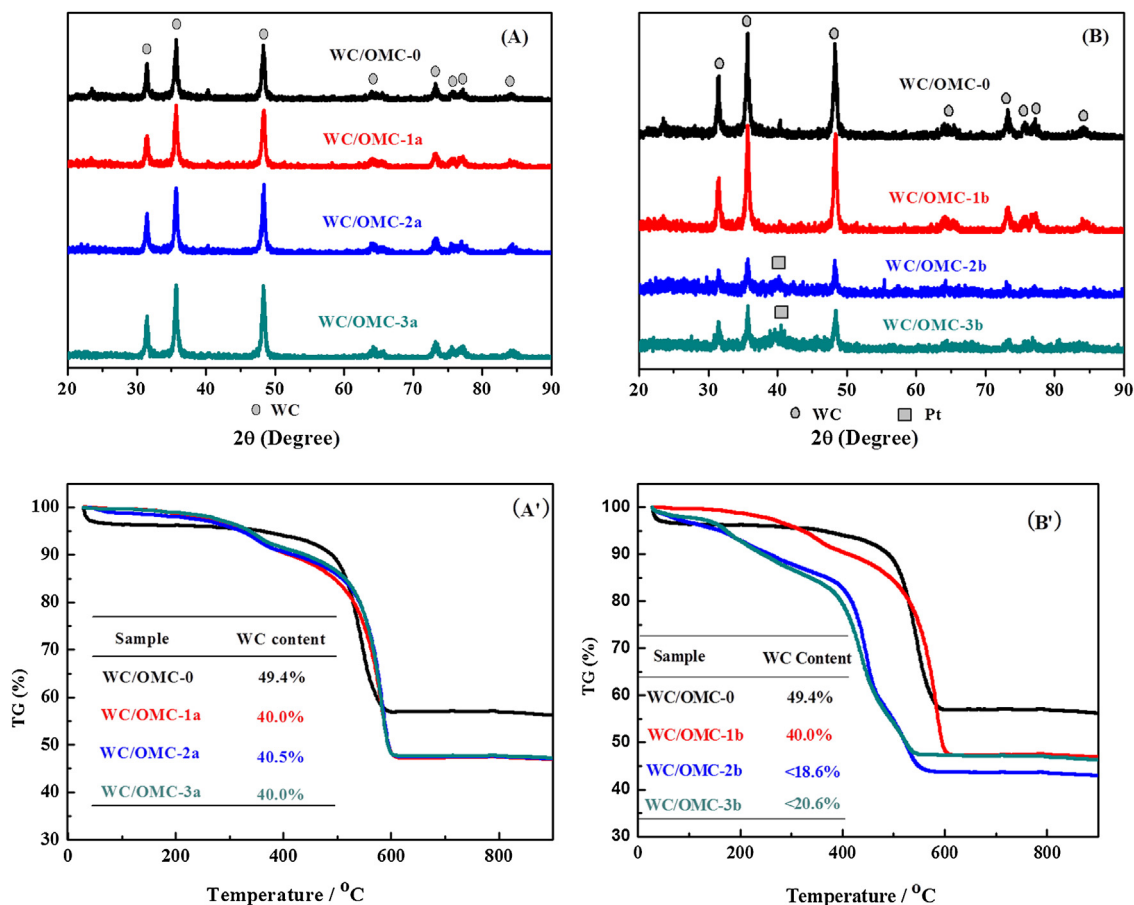
Fig. 5. XRD (A, B) and TG thermogravimetric curves (A′, B′) of the treated WC/OMC samples as shown in Fig. 2.

different WC content ($Pt_{20}@WC_{17}/OMC$-MM, $Pt_{20}@WC_{22}/OMC$-MM and $Pt_{20}@WC_{27}/OMC$-MM) were prepared and evaluated for MOR. The CV results for MOR (Fig. 9A) clearly indicate that $Pt_{20}@WC_{22}/OMC$ outperforms the other two samples, with a higher electrocatalytic peak current ($488\,mA\,mg_{Pt}^{-1}$). This behavior could be due to the bigger electrochemical surface area in the case of $Pt_{20}@WC_{22}/OMC$-MM. This can be clearly seen from the obviously bigger reduction peak of platinum oxide, shown in Fig. 9B.

Moreover, the lower MOR performance on $Pt_{20}@WC_{27}/OMC$-MM could be due to the amount of WC which has low efficiency of synergistic effect [51]. Furthermore, in the case of high WC content, because of its high density, it is difficult to prepare the well-dispersed catalyst ink and the catalyst particles are accessible to settle. In this way, the catalyst thin film could be not so good compared with the others, and thus probably leading to the inferior performance.

As far as the $Pt_{20}@WC_{17}/OMC$-MM is concerned, probably it has lower WC content, resulting in weaker synergistic effect on Pt, so its

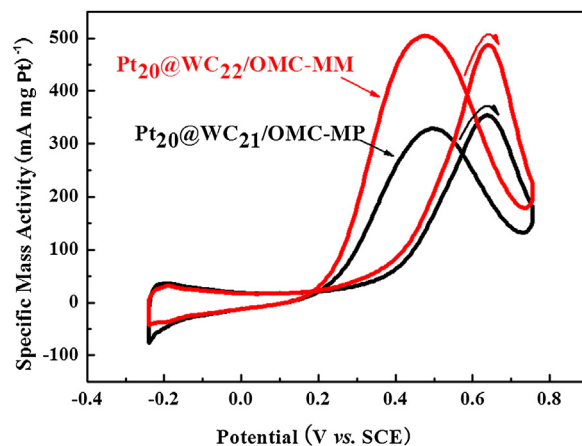**Fig. 6.** Deconvoluted W_{4f} spectra in the Pt@WC/OMC sample prepared by the pulse microwave assisted polyol method.

Fig. 7. Cyclic voltammograms of methanol electrooxidation on $Pt_{20}@WC_{22}/OMC$-MM and $Pt_{20}@WC_{21}OMC$-MP in $0.5\,mol\,L^{-1}$ $H_2SO_4 + 1.0\,mol\,L^{-1}$ CH_3OH solution. Scan rate: $50\,mV\,s^{-1}$.
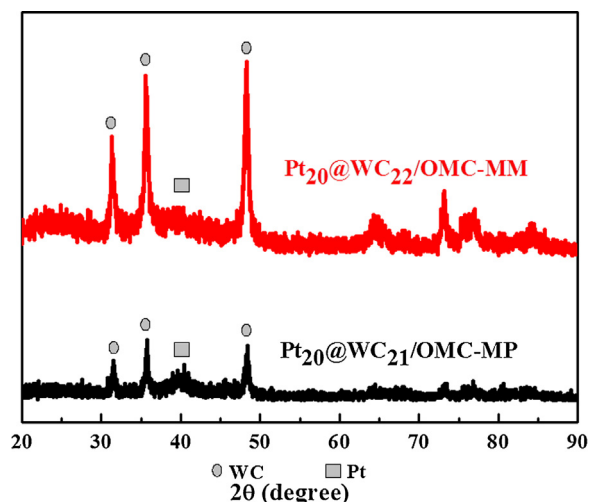
Fig. 8. XRD patterns of the $Pt_{20}@WC_{22}/OMC$-MM and $Pt_{20}@WC_{21}/OMC$-MP samples.
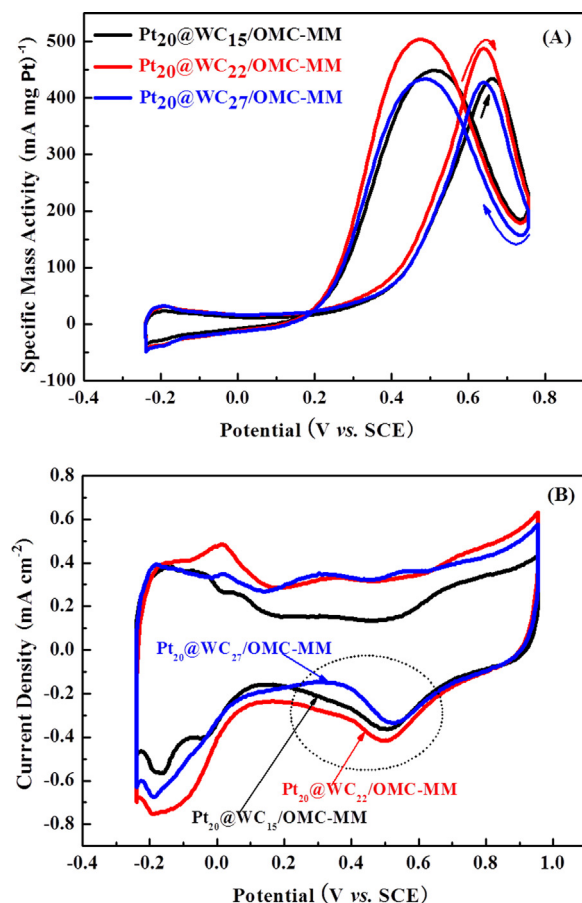
Fig. 9. Cyclic voltammograms of methanol electrooxidation on $Pt_{20}@WC_{15}OMC$, $Pt_{20}@WC_{22}/OMC$, and $Pt_{20}@WC_{27}/OMC$ obtained through mechanically mixing WC/OMC and Pt@C in $0.5\,mol\,L^{-1}$ H_2SO_4 + $1.0\,mol\,L^{-1}$ CH_3OH solution (scan rate: $50\,mV\,s^{-1}$) (A) and in $0.5\,mol\,L^{-1}$ H_2SO_4 (scan rate: $20\,mV\,s^{-1}$) (B).

4. Conclusions

In the present work, the stability of WC during the WC/OMC supported Pt-based catalysts preparation process through a pulse microwave-assisted polyol method was investigated by XRD technique and TG method.

In summary, the following conclusions can be drawn:

Acidic or alkaline environment during the above-mentioned catalysts preparation process has a little impact on WC stability.

Microwave irradiation in the presence of Pt precursor can significantly lower the stability of WC. This finding is of vital importance to realize that WC is seriously unstable during the specific catalysts preparation process.

The degree of crystallization and content of WC could obviously affect the activity of Pt toward methanol electrooxidation reaction.

In order to maximize the synergistic effect of WC supported electrocatalysts, it is necessary and important to identify and then avoid or improve the operation parameters affecting WC stability not only during the application of WC but also during catalysts preparation process.

References

[1] R.B. Levy, M. Boudart, Science 181 (1973) 547–549.
[2] J.L. Lu, Z.H. Li, S.P. Jiang, P.K. Shen, L. Li, J. Power Sources 202 (2012) 56–62.
[3] H. Zheng, Z. Chen, Y. Li, C.a. Ma, Electrochim. Acta 108 (2013) 486–490.
[4] W. Zhu, A. Ignaszak, C. Song, R. Baker, R. Hui, J. Zhang, F. Nan, G. Botton, S. Ye, S. Campbell, Electrochim. Acta 61 (2012) 198–206.
[5] A. Brouzgou, S.Q. Song, P. Tsiakaras, Appl. Catal. B: Environ. 127 (2012) 371–388.
[6] H. Lv, T. Peng, P. Wu, M. Pan, S. Mu, J. Mater. Chem. 22 (2012) 9155–9160.
[7] J.B. Christian, S.P.E. Smith, M.S. Whittingham, H.D. Abruña, Electrochem. Commun. 9 (2007) 2128–2132.
[8] M.K. Jeon, H. Daimon, K.R. Lee, A. Nakahara, S.I. Woo, Electrochem. Commun. 9 (2007) 2692–2695.
[9] D.R. McIntyre, G.T. Burstein, A. Vossen, J. Power Sources 107 (2002) 67–73.
[10] Y. Kimmel, D. Esposito, R. Birkmire, J. Chen, Int. J. Hydrogen Energy 37 (2012) 3019–3024.
[11] Y. Wang, S. Song, P.K. Shen, C. Guo, C.M. Li, J. Mater. Chem. 19 (2009) 6149–6153.
[12] Y. Wang, C. He, A. Brouzgou, Y. Liang, R. Fu, D. Wu, P. Tsiakaras, S. Song, J. Power Sources 200 (2012) 8–13.
[13] R. Ganesan, J.S. Lee, Angew. Chem. Int. Ed. 117 (2005) 6715–6718.
[14] Z.-Y. Wu, P. Chen, Q.-S. Wu, L.-F. Yang, Z. Pan, Q. Wang, Nano Energy 8 (2014) 118–125.
[15] Y. Wang, S. Song, V. Maragou, P.K. Shen, P. Tsiakaras, Appl. Catal. B: Environ. 89 (2009) 223–228.
[16] V.M. Nikolic, D.L. Zugic, I.M. Perovic, A.B. Saponjic, B.M. Babic, I.A. Pasti, M.P. Marceta Kaninski, Int. J. Hydrogen Energy 38 (2013) 11340–11345.
[17] G. Zhong, H. Wang, H. Yu, F. Peng, Fuel Cells 13 (2013) 387–391.
[18] X. Ma, H. Meng, M. Cai, P.K. Shen, J. Am. Chem. Soc. 134 (2012) 1954–1957.
[19] S. Yin, M. Cai, C. Wang, P.K. Shen, Energy Environ. Sci. 4 (2011) 558–563.
[20] H. Lv, S. Mu, N. Cheng, M. Pan, Appl. Catal. B: Environ. 100 (2010) 190–196.
[21] H. Lv, N. Cheng, T. Peng, M. Pan, S. Mu, J. Mater. Chem. 22 (2012) 1135–1141.
[22] C.J. Barnett, G.T. Burstein, A.R.J. Kucernak, K.R. Williams, Electrochim. Acta 42 (1997) 2381–2388.
[23] H. Chhina, S. Campbell, O. Kesler, J. Power Sources 164 (2007) 431–440.
[24] M.B. Zellner, J.G. Chen, Catal. Today 99 (2005) 299–307.
[25] A. Serov, C. Kwak, Appl. Catal. B: Environ. 90 (2009) 313–320.
[26] E.C. Weigert, D.V. Esposito, J.G. Chen, J. Power Sources 193 (2009) 501–506.

mass activity for MOR is lower than that on $Pt_{20}@WC_{22}/OMC$-MM. For all electrocatalysts, the backward specific mass peak current density presents the same value with the respective forward peak ($I_{forward}/I_{backward} \approx 1$), indicating their good tolerance to the formed intermediates as well as good activity toward MOR [3,52].

[27] M. Shao, B. Merzougui, K. Shoemaker, L. Stolar, L. Protsailo, Z.J. Mellinger, I.J. Hsu, J.G. Chen, J. Power Sources 196 (2011) 7426–7434.
[28] H. Chhina, S. Campbell, O. Kesler, J. Power Sources 179 (2008) 50–59.
[29] R. Ganesan, D.J. Ham, J.S. Lee, Electrochem. Commun. 9 (2007) 2576–2579.
[30] Y. Hara, N. Minami, H. Matsumoto, H. Itagaki, Appl. Catal. A: Gen. 332 (2007) 289–296.
[31] J. Regalbuto, Catalyst Preparation: Science and Engineering, Taylor & Francis Group Ltd, Oxford, UK, 2006.
[32] D.W. McKee, F.J. Norton, J. Phys. Chem. 68 (1964) 481–489.
[33] A.S. Aricò, Z. Poltarzewski, H. Kim, A. Morana, N. Giordano, V. Antonucci, J. Power Sources 55 (1995) 159–166.
[34] Z. Zhou, S. Wang, W. Zhou, G. Wang, L. Jiang, W. Li, S. Song, J. Liu, G. Sun, Q. Xin, Chem. Commun. (2003) 394–395.
[35] W.J. Zhou, S.Q. Song, W.Z. Li, G.Q. Sun, Q. Xin, S. Kontou, K. Poulianitis, P. Tsiakaras, Solid State Ionics 175 (2004) 797–803.
[36] Z. Liu, J.Y. Lee, W. Chen, M. Han, L.M. Gan, Langmuir 20 (2003) 181–187.
[37] S. Song, Y. Wang, P.K. Shen, J. Power Sources 170 (2007) 46–49.
[38] S. Komarneni, D. Li, B. Newalkar, H. Katsuki, A. Bhalla, Langmuir 18 (2002) 5959–5962.
[39] W. Chen, J. Zhao, J.Y. Lee, Z. Liu, Mater. Chem. Phys. 91 (2005) 124–129.
[40] W.-X. Chen, J.Y. Lee, Z. Liu, Mater. Lett. 58 (2004) 3166–3169.
[41] W.X. Chen, J.Y. Lee, Z. Liu, Chem. Commun. (2002) 2588–2589.
[42] S. Song, J. Liu, J. Shi, H. Liu, V. Maragou, Y. Wang, P. Tsiakaras, Appl. Catal. B: Environ. 103 (2011) 287–293.
[43] R. Ryoo, S.H. Joo, M. Kruk, M. Jaroniec, Adv. Mater. 13 (2001) 677–681.
[44] Y. Meng, D. Gu, F. Zhang, Y. Shi, H. Yang, Z. Li, C. Yu, B. Tu, D. Zhao, Angew. Chem. Int. Ed. 117 (2005) 7215–7221.
[45] F. Su, Z. Tian, C. Poh, Z. Wang, S. Lim, Z. Liu, J. Lin, Chem. Mater. 22 (2009) 832–839.
[46] C. He, Y. Liang, R. Fu, D. Wu, S. Song, R. Cai, J. Mater. Chem. 21 (2011) 16357–16364.
[47] A. Mozalev, V. Khatko, C. Bittencourt, A.W. Hassel, G. Gorokh, E. Llobet, X. Correig, Chem. Mater. 20 (2008) 6482–6493.
[48] M.B. Zellner, J.G. Chen, Surf. Sci. 569 (2004) 89–98.
[49] J. Luthin, C. Linsmeier, Surf. Sci. 454–456 (2000) 78–82.
[50] J. Zeng, C. Francia, C. Gerbaldi, V. Baglio, S. Specchia, A.S. Aricò, P. Spinelli, Electrochim. Acta 94 (2013) 80–91.
[51] Z. Yan, G. He, M. Cai, H. Meng, P.K. Shen, J. Power Sources 242 (2013) 817–823.
[52] J. Wu, Y. Xu, M. Pan, W. Ma, H. Tang, Chin. Sci. Bull. 54 (2009) 1032–1036.